

SCIENCE FOR CERAMICS PRODUCTION

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CURRENT CLASSIFICATION OF CERAMIC SILICATE PIGMENTS (REVIEW)

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The basic trends in production of ceramic pigments based on silicates of different crystal structure are examined. The features of synthesis of the pigments and formation of chromophore phases are demonstrated. The use of natural silicate and aluminosilicate materials will allow expanding the raw materials base, reduce the temperature of synthesis, and produce pigments of a broader palette for decorating porcelain and faience articles.

S. G. Tumanov proposed the current classification of ceramic pigments [1], basing it on the crystal structures of refractory, chemically stable minerals of the spinel, corundum, baddeleyite, garnet, and other types. The chromophore ions Co^{2+} , Ni^{2+} , Cr^{3+} , Fe^{3+} , V^{3+} , and Mn^{3+} , whose properties (radius and charge) are close to the ions replaced in the structure of the lattice, can be incorporated in these crystal structures in high-temperature synthesis. This approach made it possible to use purposeful synthesis to obtain a broad palette of ceramic pigments.

However, the raw-material base for synthesis of ceramic pigments has expanded significantly in recent years, which will allow refining the structural approach and proposing new variants for pigment synthesis. In particular, the use of silicates and aluminosilicates of different structures as raw materials has increased significantly [2–5]. The solid-phase reactions take place at relatively low temperatures. Not only incorporation of transition element ions in the crystal structures of silicates but also formation of chromophore phases, the products of the reaction, take place during synthesis of pigments.

The silicates used in synthesis of pigments can be divided into two groups [6]:

silicates with silica motifs of finite size:

with isolated $[\text{SiO}_4]^{4-}$ tetrahedrons (island structures);

with groups of $[\text{SiO}_4]^{4-}$ tetrahedrons of finite size;

silicates with silica motifs of infinite size in one or more directions:

with like chains or ribbons of $[\text{SiO}_4]^{4-}$ tetrahedrons (chain or ribbon structures);

with two-dimensional layers of $[\text{SiO}_4]^{4-}$ tetrahedrons (layered structures);

with three-dimensional backbones of $[\text{SiO}_4]^{4-}$ tetrahedrons (backbone structures).

Island structures have minerals of the olivine (forsterite, fayalite), garnet (grossularite), monticellite, akermanite, rankinite, and other groups.

Pigments with the structure of forsterite, $2\text{MgO} \cdot \text{SiO}_2$, were synthesized by partial substitution of MgO by CoO, and NiO and $[\text{SiO}_4]^{4-}$ tetrahedrons by Fe_2O_3 , Cr_2O_3 [7]. In incorporation of CoO in the structure of forsterite, pink to purple pigments are obtained as a function of the amount of coloring oxide [8], and in incorporation of NiO, the pigment is green. Incorporation of Fe_2O_3 decreased the synthesis temperature and increased the degree of sintering. Judging by the absorption spectra, partial incorporation of $[\text{CoO}_6]$ in the crystal structure of forsterite instead of $[\text{MgO}_6]$ took place. The green coloring of nickel-containing forsterite is due to formation of Ni_2SiO_4 and $[\text{NiO}_6]$.

Pigments of forsterite structure and pigments with the structure of magnesium metasilicate and diopside were obtained with natural minerals using talc. It is emphasized in [9] that use of the crystal lattices of natural minerals makes it possible to utilize a large number of coloring ions, which allows obtaining a wide palette of pigments. In particular, when talc is used with charge-adjusting MgO, the forsterite formation reaction can take place:



Instead of magnesium oxide, other MeO oxides (CoO, NiO, MnO) can be incorporated for charge adjustment. This

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makes it possible to synthesize a wide palette of pigments ranging from light pink to lilac and purple and from green to olive in color:



Forsterite, magnesium metasilicate, cristobalite, and coloring oxides have been identified in the diffraction pattern of the pigments obtained.

Three polymorphous modifications are known for magnesium metasilicate: protoenstatite, clinoenstatite, and enstatite [6]. Protoenstatite is the stable form and is stable at temperatures above 1010°C. Conversion into enstatite at 1300°C is characteristic of clinoenstatite. It becomes possible to incorporate coloring ions with an ionic radius close to Mg^{2+} in the crystal lattice of protoenstatite of rhombic syngony due to transformations and transitions of different forms of magnesium metasilicate. Pigments from low-temperature synthesis are obtained, while forsterite Mg_2SiO_4 is a high-temperature compound which melts congruently at 1890°C and does not form polymorphic modifications.

The structure of forsterite is characterized by isolated $[\text{SiO}_4]^{4-}$ tetrahedrons with Mg^{2+} ions between them. When the latter are substituted by Fe^{2+} , olivine $(\text{Mg}, \text{Fe})\text{SiO}_4$ is formed [10]. Partial substitution of MgO by ZnO changes the crystal structure of forsterite and the willemite phase appears with characteristic diffraction peaks in the diffraction pattern. The transition to the new structure intensifies the chromophoric properties of the synthesized pigments, while pigments based on forsterite alone have a pale, subdued tint.

Pigments of different color scales are obtained in synthesis of pigments using willemite and garnet island silicates. It is noted in [11–13] that when other coloring oxides are added to cobalt-containing willemite, the color of the pigment changes. Incorporation of a large amount of NiO causes the formation of green nickel orthosilicate Ni_2SiO_4 together with willemite, so that the color of the pigments is dark blue with a green hue.

Brightly colored pigments have been synthesized from garnet structures [14, 15]. Synthesis was conducted with CoO , NiO , CuO , MnO , Cr_2O_3 , and Fe_2O_3 in the presence of the mineralizers B_2O_3 and Li_2O . Pale pink, dark green, turquoise, yellow, and pigments of other colors were obtained as a result. Garnet pigments are resistant to the dissolving effect of fluxes and can color glass and ceramics. Equimolecular substitution of the $[\text{SiO}_4]^{4-}$ acid radical by $[\text{PO}_4]^{3-}$ with consideration of the basicity of orthophosphoric and orthosilicic acids is possible in garnets with the common formula $\text{R}_3^{2+}\text{R}_2^{3+}[\text{SiO}_4]_3$. Studying the structure of the garnet-type pigment $3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5$ confirmed that it is a ternary compound. Reflections indicating the presence of small amounts of AlPO_4 in cristobalite form were identified in the diffraction pattern.

In studying the chromic pigment of garnet structure $3\text{CaO} \cdot \text{Cr}_2\text{O}_3 \cdot \text{SiO}_2$, it was found that synthesis of the pig-

ment begins at 1000°C. CaCr_2O_4 is initially formed and then decomposes at higher temperatures. A pigment of the garnet type is formed in the reaction with the remaining compounds.

The possibility of obtaining pigments using raw materials containing magnesium, calcium, silicon, and other oxides was demonstrated as a result of these studies, using silicates of chain structure with the general formula $\text{AB}[\text{Si}_2\text{O}_6]$, augite in particular ($\text{A} = \text{Cu}^{2+}$, $\text{B} = \text{Mg}^{2+}$) [16]. The pigments are synthesized in the 750–1250°C temperature range. The brightest colors are obtained in incorporation of V_2O_5 and Cr_2O_3 together with Al_2O_3 , and the solid solutions $\text{Cr}_{2-2x}\text{Al}_{2x}\text{O}_3$ and $\text{Al}_{2-2x}\text{Cr}_{2x}\text{O}_3$, where $x < 0.2$, are formed even at temperatures of 750–850°C. The stabilizing effect of V_2O_5 due to the appearance of a crystalline phase containing CrVO_4 , CaV_2O_5 , $\text{Ca}_2\text{V}_2\text{O}_7$, and $\text{Ca}(\text{VO}_3)_2$ is noted in [17]. The presence of anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ and wollastonite CaSiO_3 was also observed.

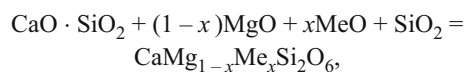
Ceramic pigments have also been synthesized from wollastonite and diopside [18, 19]. Mineral raw materials were used as the initial components. Substitution of Mg^{2+} by Co^{2+} and Si^{4+} by Fe^{3+} , Ti^{4+} , V^{3+} , Cr^{3+} , and especially Al^{3+} is possible in diopside $\text{CaMgSi}_2\text{O}_6$, which has a pyroxene structure. As the published data show, this is because the ionic radius of Al^{3+} (0.57 Å) and ratio $r_c : r_a = 0.43$ in Al_2O_3 (r_c and r_a are the ionic radii of the cation and anion) enable formation of four- and six-coordinated $[\text{AlO}_4]^{5-}$ and $[\text{AlO}_6]^{9-}$ structures [20]. The brightest dark-blue-light-blue pigment is obtained at a mass ratio of (%): 0.80–1.00 CaO , 0.05–0.10 MgO , 0.05–0.80 CoO , 0.30–0.50 SiO_2 , 1.20–1.50 Al_2O_3 [19].

When NiO is incorporated in diopside instead of MgO , pigments whose color ranges from lettuce-green to dark green are obtained. If MnO , Fe_2O_3 , and V_2O_5 are added to diopside, a broad palette of pigments in which the color-bearing phase is a spinel and partially does not react with coloring oxides can be obtained at relatively low temperatures.

Pigments with the crystal structure of diopside were synthesized from natural wollastonite with addition of MgO and SiO_2 in heat treatment [18]:



In addition of chromophoric MeO oxides to diopside, a colored diopside is formed:

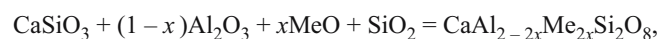


where $x = 0.1 - 1.0$ mole.

Soluble transition metal salts can be used instead of MeO [18]. At 1200°C, diopside, wollastonite residues, and MgFe_2O_4 and MgCr_2O_4 colored spinels are found in the cake if the concentration of iron and chromium oxides is less than 0.5 mole.

The effect of the mineralizing additives boric acid and topaz $\text{Al}_2\text{SiO}_4(\text{F}, \text{OH})_2$ on synthesis of ceramic pigments was investigated in [20]. It was found that these mineralizers stimulate formation of a liquid phase containing artificial crystallization nuclei, rearrangement of the crystal structure, and formation of solid solutions at 900–1200°C. Not only the temperature of synthesis but also the polarizability of the oxygen ions in $[\text{CoO}_4]$, $[\text{CoO}_6]$, $[\text{NiO}_4]$, $[\text{NiO}_6]$, and other coloring complexes decrease in the presence of B^{3+} and F^- ions, which intensifies the absorption bands in the visible region of the spectrum and increases the brightness of the pigments.

The slit diffraction patterns of pigments synthesized from wollastonite contain reflections belonging to diopside and anorthite. The intensity of the diopside reflections increases in the presence of mineralizers, which indicates formation of solid solutions. A backbone structure represented by $[\text{SiO}_4]$ and $[\text{AlO}_4]$ tetrahedrons is characteristic of anorthite $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, and the gaps between them are filled with Ca^{2+} cations, which ensures a continuous series of solid solutions according to the scheme in [18]:



where MeO are coloring oxides.

In the opinion of the investigators in [18], pigments with an anorthite structure of complex composition containing anorthite and wollastonite are obtained as a result of synthesis. When Cr_2O_3 and Fe_2O_3 are added in amounts above 16%, reflections belonging to helenite $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, which is transformed into anorthite above 1200°C, are identified in the diffraction pattern.

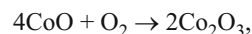
Pigments of anorthite structure formed through an intermediate phase of helenite are obtained in synthesis of pigments using CaO , Al_2O_3 , and SiO_2 contained in anorthite at temperatures above 1200°C. Solid solutions with isomorphic substitution of the oxides in anorthite by transition metal oxides, which allows obtaining a broad palette of pigments, are formed in the presence of 1.5% NaF [21]. The colored spinel CoAl_2O_4 has also been identified.

SiO_2 , Al_2O_3 [22], and raw materials, kaolin in particular [23], were used as initial materials in synthesis of pigments of mullite-like structure. Partial or total substitution of the Al_2O_3 in mullite by Cr_2O_3 was conducted to study the possibility of synthesizing such pigments. Green pigments were obtained as a result. The possibility of formation of chromium-containing mullite $3(\text{Al}, \text{Cr})_2\text{O}_3 \cdot 2\text{SiO}_2$ and $(\text{Al}, \text{Cr})_2\text{O}_3$ solid solution was established with thermodynamic calculations.

The studies on finding ways of synthesizing pigments based on natural kaolin demonstrated the possibility of obtaining pigments with the structure of mullite. Colored mullite, corundum, and transition metal orthosilicates can be obtained in the presence of mineralizers and the impurities contained in kaolin.

In synthesis of pigments using silica, it was found that the coloring phase consists of transition metal silicates. In particular, in addition of CoO in the presence of B_2O_3 , quartz, cristobalite, and Co_2SiO_4 are found. The pigment has elevated chromophoric characteristics: 26.3% brightness, 10% saturation, and 554 nm dominant wavelength [24].

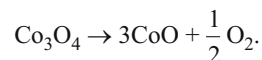
The change in the phase composition during heat treatment was investigated to determine the mechanism of formation of cobalt-containing silicate pigments. At 800°C, Co_3O_4 with a crystal lattice of the $\text{Co}^{2+}[\text{Co}^{3+}]_2\text{O}_4$ spinel type was identified in the diffraction pattern. The following reaction takes place in the first stage:



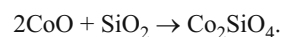
and in the second stage:



In the 1000–1100°C temperature range, Co_3O_4 of rhombic structure is formed, followed by decomposition:



Cobalt oxide interacts with the silicate base and forms the color-bearing phase:



Mineralizers, Li_2CO_3 in particular, affect the color characteristics. The role of lithium ions is reduced to compensation of the electrostatic charge in the crystal lattice and provides for the stability of the structure of the pigment and increases the quantity of silicate melt.

Pigments containing oxide residues and orthosilicates, NiO and Ni_2SiO_4 , for example, are formed with other coloring oxides. Amorphous silica gel – a chemical plant waste – can be used instead of silica.

Use of natural silicate minerals can thus serve as the basis for synthesis of a broad palette of ceramic pigments at comparatively low temperatures. It then becomes possible to use local raw materials and industrial wastes.

The reported data indicate that even with the limited ion capacity of natural crystal structures, material with new structures suitable for production of quality ceramic pigments with less power-consuming technology and use of readily available raw materials can be synthesized.

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